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Let us now return to the action of bile upon fats. After I had observed the property of phosphate of soda of emulsioning fatty acid, and not neutral fats, it struck me that bile might be possessed of a similar power, which I found to be the case; and, after giving this important subject all the attention it deserved, the results of my enquiries were communicated to the Royal Society in 1858. Shortly afterwards I was informed that bile had already been observed by Lenz, of Dorpat, to possess the abovementioned property; and, by referring to his valuable Dissertation "On the Digestion of Fats," I found that he was the first who discovered, so far back as 1850, that bile emulsioned fatty acids, but not neutral fats; he also noticed that the emulsion was attended with the formation of soap, and I readily avail myself of this opportunity of acknowledging the fact.

I cannot find that Lenz conducted his experiments with other fats than oil. I employed the solid fats of meat, which are those usually taken into the stomach; my attention was especially directed to the quantitative analysis of the emulsion, in order to determine the proportions of soap and fatty acids it contained; and finally I discovered this remarkable and interesting fact, that if the mother-liquor in which the emulsion is suspended be filtered from the emulsioned fat, it is capable, notwithstanding its strongly acid reaction, of forming more soap and emulsioning more fatty acid, although before filtration the saponification had been entirely arrested; the filtrate from this second operation is likewise capable of effecting a further saponification and emulsion, but the action is less and less powerful; in one series of experiments, the proportions of fatty acids saponified were 20·5 %, 12·7 %, and 3·8 % of those experimented on.

The importance of the change which neutral fats undergo in the stomach will now be readily understood; for it is indispensable to their subsequent emulsion in the intestines by the bile, under which form they are absorbed. I do not wish, however, to attribute to bile exclusively the power of digesting fats: for I fully believe that a portion of the fats taken into the stomach is not acidified, and, consequently, must escape the action of the bile; in this case the pancreatic juice effects the required emulsion. It is remarkable that in both cases the fats are absorbed in great measure under the form of emulsioned fatty acids; for it is now generally admitted that the pancreatic juice has the power of acidifying neutral fats, as was discovered by Prof. Bernard.

This absorption of fatty acids explains a fact I observed, with Mr. Verdeil, while at work in Messrs. Wurtz and Verdeil's laboratory at Paris, in 1851—namely, that blood contains free fatty acids.

The alimentary canal is so perfectly adapted to the functions of digestion, that notwithstanding the great variety of food taken, and the amount of nourishment ingested, which is frequently much greater than that strictly required for the maintenance of the body, only a very small proportion of food passes off in the evacuations in the healthy state; they may be said to contain no element of food soluble in water, for they merely yield to water a small quantity of an albuminous substance possessed of the characters of the albumin of the pancreatic juice, which in all probability it is. Under the microscope, we find in the alvine dejections, a few fragments of muscular tissue, from the meat taken, and the hairs of wheat ingested with bread; a few cells and fibres are all that remains of vegetable food. None of the fats of food are found therein in the free state, but the evacuations contain small quantities of phosphate of soda, soda soaps, and a larger proportion of earthy phosphates and earthy soaps.

The principal object of the alvine evacuation is obviously to rid the body of certain parts of the intestinal secretions, which, after having served their purpose in effecting the digestion of food, are not fit to return into the blood. It is very difficult to trace the connection of these excreted substances with the various intestinal secretions; in this respect, we must at present rest satisfied with probabilities. Among these various substances there is one of great interest, I have called *excretin* [$C_{78}H_{78}O_2S$.]. This substance, which has been fully described elsewhere,* crystallises from its alcoholic or ethereal solution, exhibiting beautiful silky crystals, which are acicular four-sided prisms. In its properties it closely resembles *cholesterin*, being soluble in hot alcohol and ether, sparingly soluble in cold alcohol, insoluble in water, and not saponifiable; like cholesterin, it dissolves in small quantity in the bile. It has also some physiological connection with chlolesterin, as I have found the excreta of very young children to contain no excretin, but chlolesterin, whilst it is the reverse in the case of young people and adults. On this account, I believe excretin to be a constituent of the bile.

* Phil. Trans., 1854, ii, 265.

L.—*On the Hydrides of the Alcohol-radicles existing in the Products of the Destructive Distillation of Cannel Coal.*

By C. Schorlemmer,

Assistant in the Laboratory of Owens College, Manchester.

The light oils produced in the destructive distillation of coal have lately found so extended an application in the arts, that the yield of these oils, in the process of gas-making, has proved quite insufficient to meet the trade demand.

Considerable quantities of coal are, therefore, now distilled with the sole object of obtaining liquid products. The yield of volatile liquid depends, as is well known (1), upon the circumstance that the distillation is conducted at as low a temperature as possible, and (2) that the substances, when once formed, are not decomposed by exposure to a red heat.

Mr. John Barrow, of the Dalton Chemical Works, Gorton, near Manchester, has been kind enough to place a sufficient quantity of the light oils obtained by the distillation of coal at my disposal, to enable me to undertake a thorough examination of their chemical composition. They are obtained by Mr. Barrow, on the large scale by distilling Wigan Cannel in retorts, the lower surfaces of which are heated, whilst the upper parts are kept as cool as possible.

The crude oil possesses the peculiar smell of the compound ammonias, and when these are removed by treating the liquid with dilute sulphuric acid, the oil assumes the peculiar garlic-like smell of the higher olefines.

On submitting the oil to repeated fractional distillation, a small quantity of liquid is obtained boiling below 20° C., a considerable quantity distils between 35°—45° C., much less from 45°—65°, whilst above 65° about equal portions distil for every 5° of increase of temperature. It was, however, found impossible to obtain a product of constant boiling point by repeated fractional distillations.

When concentrated nitric acid is brought in contact with the

oil, so violent an oxidation occurs, that spontaneous ignition of the more volatile portions of the oil sometimes takes place. When the action is moderated by cooling, a large portion of the oil remains unacted upon, whilst considerable quantities of nitro-compounds are formed.

I confine myself, in the present communication, to the consideration of the liquids which remain unacted upon by nitric acid, and are contained in the crude oil boiling below 120° C.

The separation of these oils by means of nitric acid is a tedious and disagreeable operation. It may, however, be easily effected by previously shaking up the crude oil with an equal volume of ordinary sulphuric acid. The mixture becomes heated, assumes a dark colour, and gives off a smell resembling that of peppermint, and after some time sulphurous acid is evolved.

The liquids were allowed to remain in contact for several days, and were frequently shaken; the oil was then poured off, washed with water and distilled, a large quantity of tarry matter being left behind in the retort.

The distillate consisted mainly of benzol and toluol, together with the liquids unacted upon by acids. For the purpose of obtaining the latter liquids in the pure state, I have employed the method described by Greville Williams in his researches on the hydrocarbons from Boghead coal.* This method consists in repeatedly shaking the oil with concentrated nitric acid, until, on addition of water to the acid liquid, no further separation of nitro-compounds occurs. The liquid unacted upon is then washed with water, dried over potash, and repeatedly rectified over sodium.

By fractional distillation of this liquid, the following four bodies were obtained—

C_5H_{12}	boiling point	39— 40° C.
C_6H_{14}	„	68— 70° „
C_7H_{16}	„	98— 99° „
C_8H_{18}	„	119—120° „

It will be shown that these liquids are the hydrides of the alcohol-radicles, inasmuch as they have been transformed by the action of chlorine into their corresponding chlorides.

* Phil. Transact., 1857.

(1) *Hydride of Amyl:* C_5H_{12}.

Analysis: 0·1870 substance gave 0·5715 carbonic acid and 0·2810 water.

		Calculated.	Found.
C_5	60	83·33	83·3
H_{12}	12	16·67	16·7
	72	100·00	100·0

Determination of Vapour-density.

(*a*)	Substance taken	0·1010 grm.
	Temperature of air	16°·0 C.
	Temperature of vapour.....	55°·0 C.
	Volume of vapour.....	54°·8 cbc.
	Height of barometer.....	752°·0 mm.
	Difference of level	235°·5 mm.

The density calculated from these numbers is 2·523.

(*b*)	Temperature of vapour.... .	66°·0 C.
	Volume of vapour.....	56°·0 cbc.
	Difference of level.....	230°·0 mm.

Hence the vapour-density = 2·519.

(*c*)	Temperature of vapour.....	91°·0 C.
	Volume of vapour.....	59°·5 cbc.
	Difference of level.....	220°·0 mm.

These numbers give the density of 2·497, closely corresponding to the theoretical density 2·493 of hydride of amyl.

Hydride of amyl is thin mobile liquid, boiling between 39 and 40° C., and possessing a pleasant smell, resembling that of chloroform. Sp. gr. = 0·636 at 17° C. It burns with a bright, luminous, non-fuliginous flame. These properties, with the exception of the boiling point, correspond with those of the hydride of amyl, as described by Frankland. Although a small portion of the purified oil distils over below 30° C., I

did not succeed, after repeated fractional distillations, in obtaining a liquid having a constant boiling of 30° C., as found by Frankland, by far the greatest part of the liquid distilling between 39—40° C.

Greville Williams has lately shown the presence of hydride of amyl in the oils obtained by the destructive distillation of Boghead coal.*

(2) *Hydride of Hexyl (Caproyl)* : C_6H_{14}.

Analysis: 0·1460 substance gave 0·4490 carbonic acid, and 0·2135 water.

	Calculated.		Found.
C_6	72	83·72	83·8
H_{14}	14	16·28	16·3
	86	100·0	100·1

Determination of Vapour-density.

Balloon with air	23°·449 grms.
Temperature of air	15°·5 C.
Balloon with vapour.....	23°·720 grms.
Temperature on sealing	110°·0 C.
Capacity of balloon.....	178°·0 cbc.

Hence the vapour-density = 2·98; the theoretical-density of hydride of hexyl is 2·98.

Hydride of hexyl is a thin mobile liquid, of a faint but pleasant smell, burning with a luminous, slightly smoky flame. Boiling point 68—70° C. Sp. gr. at 15°·5 = 0·678.

There can be little doubt that the body, possessing the same composition and boiling point, which Greville Williams found in the oils from Boghead coal, described in his first paper as propyl, is really hydride of hexyl. Cahours and Pelouze have lately shown that it is contained in large quantities in the American rock oil.†

* Journ. Chem. Soc. xv., 130. † Phil. Trans., 1857.

3. *Hydride of Heptyl (Oenanthyl)* : C_7H_{16}.

Analysis :—0·1765 substance gave 0·5440 carbonic acid and 0·2570 water.

	Calculated.	Found.
C_7	84·0	84·0
H_{16}	16·0	16·1
	100·0	100·1*

Determination of Vapour-density.

Balloon with air.....	24°·368 grms.
Temperature of air.....	18°·0 C.
Balloon with vapour	24°·671 grms.
Temperature on sealing.....	150°·0 C.
Capacity of balloon	179°·0 cbc.
Residual air	0°·3 cbc.

These numbers give the vapour-density..... = 3·49
The theoretical density of hydride of heptyl is = 3·46

Hydride of heptyl is a liquid closely resembling hydride of hexyl; it possesses a similar smell, and burns likewise with a slightly smoky flame. Boiling point 98—99° C. Specific gravity at 17·5° = 0·709.

When chlorine is passed into hydride of heptyl, the liquid becomes warm, and hydrochloric acid is given off. The substitution-products formed are partially decomposed by distillation; hydrochloric acid is evolved, and carbon separates out, and the distillates assume green, blue, or purple colours, which disappear after standing for some time. A large portion however of the chlorinated liquid distils without decomposition; and from this portion, when the treatment with chlorine has not been carried too far, a considerable quantity is obtained by fractional distillation, boiling between 150—152° C (not corrected). This body possesses the composition and properties of chloride of heptyl $C_7H_{15}Cl$.

Analysis: The combustion was effected with oxide of copper, the front part of the tube containing copper-turnings.

* Compt. rend. liv. 1241.

0·2522 substance gave 0·5765 carbonic acid and 0·2580 water.

0·2032 substance gave 0·2120 chloride of silver and 0·0036 metallic silver.

		Calculated.	Found.
C_7	84	62·45	62·3
H_{15}	15	11·15	11·4
Cl	35·5	26·40	26·4
	134·5	100· 0	100·1

Chloride of heptyl is a colourless liquid, of a pleasant smell, burning with a smoky, green-bordered flame, and possessing the specific gravity of 0·891 at 19° C.

When it is boiled with an alcoholic solution of acetate of potassium, chloride of potassium separates out, but the decomposition goes on very slowly. When, however, the mixture is heated in sealed tubes to about 120—130° C., the chloride is completely decomposed in a few hours, and the liquid consists of an alcoholic solution of acetate of heptyl, which separates out on the addition of water, as a light oily liquid, having a strong and pleasant smell of pears. Treated with an aqueous solution of potash, this ether is easily decomposed and heptylic alcohol is formed, possessing a peculiar aromatic smell, resembling somewhat that of octylic alcohol as prepared from castor oil. I am at present engaged upon the investigation of the heptyl compounds.

Besides the chloride of heptyl, some chlorine-compounds, boiling at higher temperatures and distilling without decomposition, were formed, but the quantity was only small and I did not succeed in obtaining a product of constant boiling point. Heated with sodium, these chlorine-compounds are easily decomposed, and a liquid, free from chlorine is obtained, which boils between 95—100° C., and possesses the peculiar smell of heptylene C_7H_{14}.

Analysis: 0·1618 substance gave 0·5080 carbonic acid, and 0·2125 water.

		Calculated.	Found.
C_7	84	85·71	85·6
H_{14}	14	14·29	14·6
	98	100·00	100·2

The quantity obtained was too small for determining the vapour-density.

(4) *Hydride of Octyl (Capryl)* : C_8H_{18}.

Analysis: 0·2095 substance gave 0·6465 carbonic acid and 0·3040 water.

	Calculated.		Found.
C_8	96	84·21	84·1
H_{18}	18	15·79	16·1
	114	100·0	100·2

Determination of Vapour-density.

Balloon with air	7·098 grms.
Temperature of air	15·5° C.
Balloon with vapour.....	7·33 grms.
Temperature on sealing	170·0° C.
Capacity of balloon	119·5 cbc.

The vapour-density calculated from those numbers = 3·98
The theoretical density of Hydride of Octyl is .. = 3·95

Hydride of octyl in its physical properties closely resembles the hydrides of hexyl and heptyl. It boils at 119—120°, and has a spec. grav. of 0·719 at 17°·5.

In the above-mentioned paper on the hydrocarbons from the oil obtained by the destructive distillation of Boghead coal, Greville Williams has described as butyl, a body of the above composition and boiling point, which is doubtless hydride of octyl.

The action of chlorine on hydride of octyl is similar to the action on hydride of heptyl; a large portion of the products formed are decomposed when distilled; whilst the portion which volatilizes without decomposition, yields by fractional distillation a considerable quantity of a liquid boiling between 170—172° C. (not corrected), which possesses the composition and properties of chloride of octyl $C_8H_{17}Cl$.

Analysis: I. 0·1800 substance, gave 0·4250 carbonic acid, and 0·1895 water.

II. 0·1697 substance, gave 1635 chloride of silver, and 0·0015 metallic silver.

Analysis: III. 0·2342 substance, gave 0·2280 chloride of silver, and 0·0012 metallic silver.

	Calculated.		Found.		
			I.	II.	III.
C_8	96	64·65	64·4	—	—
H_{17}	17	11·45	11·7	—	—
Cl	35·5	23·90	—	23·9	24·2
	148·5	100·0			

Chloride of octyl is a colourless liquid, possessing a faint but pleasant smell of oranges, and burning with a smoky, green-bordered flame. Spec. grav. = 0·892,* at 18° C.

Heated with an alcoholic solution of acetate of potassium, it is decomposed in the same manner as chloride of heptyl.

The volatile chlorine-compounds which are formed together with chloride of octyl, were present in small quantity only, and I was unable to obtain a product of constant boiling point. Heated with sodium, they are easily decomposed, and I observed the formation of the blue body described by Bouis.† By repeated treatment with sodium at a higher temperature, a liquid, having a smell like that of heptylene, was obtained, boiling between 115—125° C. By fractional distillation, the greatest portion was obtained between 115—117° C. Bouis gives the boiling point of octylene at 125° C.

The analysis of the liquid boiling at 115—117° C. gave the following results:—

Substance taken.....	0·1394
Carbonic acid obtained....	0·4375
Water obtained.....	0·1845

	Calculated.		Found.
C_8	96	85·71	85·6
H_{16}	16	14·29	14·7
	112	100·00	100·3

* It appears from a number of determinations, that the spec. grav. of $C_7H_{15}Cl$ and $C_8H_{17}Cl$ are very nearly the same.

† Compt. rend xxxviii. 935.

Determination of Vapour-density.

Balloon with air	8°·0015 grms.
Temperature of air	18°·5 C.
Balloon with vapour.....	8°·1080 grms.
Temperature on sealing	177° C.
Capacity of balloon.....	51°·7 cbc.

The density calculated from these numbers is ..... 4·17,
whilst the theoretical density of octylene is .... 3·88.

I have convinced myself that the oils from Cannel coal, having a higher boiling point than those I have as yet examined, likewise contain substances unalterable by the strongest acids. There appears therefore to be little doubt that the whole series of homologous hydrides are contained in the products of the distillation of coal at low temperatures; and I would venture the suggestion that the so-called paraffins, which are likewise not acted upon by strong acids, may prove to be the higher members of the same series.

In conclusion, I beg to express my best thanks to Professor Roscoe for the valuable advice which he has given me in carrying out the above investigation.

LI.—*On Capillary Liquid Transpiration in relation to Chemical Composition.*

By Thomas Graham, F.R.S., Master of the Mint.

[From the Philosophical Transactions, 1862.]

The passage of liquids under pressure through a capillary tube is here spoken of as capillary liquid transpiration, in accordance with the analogy of gaseous transpiration. The subject owes the development which it has already acquired chiefly to the investigations of the late Dr. Poiseuille.* The precision of the results

* Mém. Savans Etrangers, ix., 433; Ann. Ch. Phys. [3], vii. and xxi.

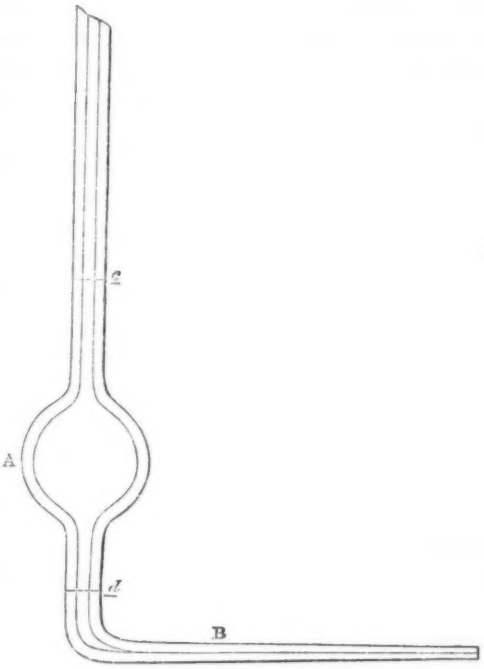
attainable by the mode of experimenting pursued by that physicist has been remarked on by every one who has followed him in the inquiry. The observations on this subject which we owe to M. Poiseuille and other inquirers are very numerous, but have not, so far as I am aware, been connected hitherto with any speculative views of the chemical or molecular constitution of liquids.

The isolated discovery of M. Poiseuille, that diluted alcohol has a point of maximum retardation, coinciding with the degree of dilution at which the greatest condensation of the mixed liquids occurs, appears to offer a starting point for new inquiries. The same result may be otherwise expressed, by saying that the definite compound of 1 equivalent of alcohol with 6 equivalents of water, $C_4H_6O_2+6HO$*, is more retarded than alcohol containing either a greater or a smaller proportion of water. The rate of transpiration appears here to depend upon chemical composition, and to afford an indication of it. A new physical property may thus become available for the determination of the chemical constitution of substances. Methylic alcohol being found to exhibit the same remarkable feature in its transpiration, although the 6-hydrate of that alcohol is not distinguished by extraordinary condensation of volume, the inquiry was extended to the hydrated acids. The results obtained with the latter substances give a certain degree of generality to the relation subsisting between the transpirability and chemical composition of liquids.

The apparatus employed was very similar to that of M. Poiseuille. It consisted of a small but rather stout glass bulb, A (see figure), about two-thirds of an inch in diameter, having a capacity of from 4 to 8 cub. cent., blown upon a thick glass tube, with a bore of about 2 millimetres. A scratch (*c*) was made upon the glass tube above, and another (*d*) below the bulb, to indicate the available capacity of the instrument. The lower tube was bent at a right angle to the upper, and a fine capillary tube, B, from 3 to 4 inches in length, was sealed to the curved extremity of the tube. The bulb and capillary were always held immersed in a vessel of water during the experiment, in order to secure uniformity of temperature. The force employed to impel the liquid through the capillary was the weight of one atmosphere of

* Halving the equivalent of alcohol, the hydrate of greatest retardation becomes $C_2H_3O + 3HO$.

760 millimetres of mercury, and was obtained from compressed air contained in a large reservoir provided with a mercurial gauge, as in Poiseuille's experiments. The time was noted in seconds which the level of the liquid in the bulb took to fall from the mark *c* to the mark *d*. This time varied from about 300 to 900 seconds in different liquids. In successive experiments made upon the same liquid, the variation in the time, or error of observation, did not exceed one or two seconds. The experiment was always repeated two or three times, and a mean taken. The temperature of the liquid transpired was always 20° C. (68° F.), when not otherwise stated.



The liquid may be introduced into the bulb through the open upper tube by means of a tube-funnel; but it was found more convenient in practice, although requiring a much longer time, to fill the bulb by aspiration through the capillary. With this view, the compressed air was shut off by a stop-cock, and the upper tube of the bulb was then allowed to communicate with the receiver of an air-pump, instead, by which exhaustion was produced, while the open end of the capillary was immersed in a portion of the liquid. The liquid which entered the bulb in this manner was sure to be free from any solid matter that could cause obstruction in the capillary during the subsequent passage of the liquid outwards, while the disconnecting of the bulb from the rest of the apparatus, for the purpose of filling the former, was also avoided.

Nitric Acid.

A bulb provided with a capillary tube, distinguished as capillary C, was used in the transpiration of nitric acid and of several other liquids. The dimensions of this bulb C were as follows:—Capacity of bulb, 8·075 cub. cent.; length of capillary tube, 28 millims.; diameter of bore, 0·0942 millim. The time of passage of water through the tube, under the pressure of one atmosphere and at the fixed temperature of 20°, was 348 seconds. The time of the passage of the most highly concentrated nitric acid through the same capillary was found to be 344·5 seconds, or slightly less than the time of water. This is the protohydrate of nitric acid, $HO.NO_5$ or NHO_6. With the addition of water to the acid, the transpiration of equal volumes of liquid becomes gradually slower; till as much as three additional equivalents of water were added, when the transpiration-time rose to its maximum, 732 seconds. The last hydrate is the well-known definite compound NHO_6+3HO, having the specific gravity 1·4, and possessing the highest boiling point of any compound of nitric acid and water. Diluted beyond this point, nitric acid begins to pass more freely, and the transpiration-time approaches again to that of water. With the addition of twice its weight of water, or about 7 equivalents, the acid passed through the capillary in 472 seconds.

The experiments made upon nitric acid are recorded in the following Table. It will be observed that the retardation is considerable for a certain distance on both sides of the maximum point. No unusual retardation appears to occur with the proportions of water corresponding to 2 and 4 equivalents. The specific gravity of the acid liquid is added in the last column of the Table, whenever that property was observed.

TABLE I.—Transpiration of Nitric Acid, at 20° C., by Capillary C.*

(Transpiration-time of water, 348 seconds.)

Water added to 100 acid (NHO_6).	Water, per cent.	Transpiration-time.		Spec. grv. at 15°.
		In seconds.	Water = 1.	
0	0	344·5	0·9899	1·5046
25·47	20·38	692	1·9885	1·4358
28·56 .. 2 eqs. HO	21·43	705	2·0258	
30	23·07	712	2·0459	
40	28·50	725	2·0833	
42·85 .. 3 eqs. HO	29·99	732	2·1034	1·3978
45	31·03	730	2·0977	
50	33·33	728·5	2·0919	1·3816
55	35·48	718	2·0632	
57·12 .. 4 eqs. HO	36·35	712	2·0459	
60	37·50	709·5	2·0387	1·3598
70	41·17	683	1·9626	1·3407
80	44·44	661	1·8994	1·3239
90	47·36	635·5	1·8261	
100	50·00	593	1·7040	1·2943
200	66·66	472	1·3563	

It appears then, that a certain hydrate of nitric acid is marked out by its low transpirability so distinctly, that nitric acid could be identified by that physical property. Such a property may prove to be typical of a class of acids to which nitric acid belongs. The hydration of nitric acid probably advances by three equivalents at a time, NHO_6+3HO, as in the magnesian nitrates, $NMO_6+3HO+3HO$. The transpiration of the assumed second hydrate of nitric acid was not made the subject of experiment. A certain steadiness is observed in the transpiration of this acid on either side of the point of maximum retardation.

* In the following tables, the particular capillary employed is in each case designated by a particular letter. Capillary C, which was more employed than any other, became reduced in length during the course of the experiments, the end being ground off on several occasions on account of the choking of the tube. This capillary is then described as C shortened. It did not seem requisite to give in every case the dimensions of the bulb and capillary tube, as all the experiments were conducted on the same plan, and the transpiration of water is in every case given as a standard of comparison. Direct experiments were also made, which proved that the transpiration-times were sensibly inversely proportional to the effective pressure applied to the liquid, as found by Poiseuille; which indicates that the capillaries offered sufficient resistance to the passage of the liquid.

Sulphuric Acid.

TABLE II.—Transpiration of Sulphuric Acid, at 20°, by Capillary G.

(Transpiration-time of water, 109 seconds.)

Water added to 100 acid (SHO_4).	Water, per cent.	Transpiration-time.		Spec. grv. at 15°.
		In seconds.	Water = 1.	
0	0	2360	21·6514	1·8456
2·5	2·43	2412	22·1284	1·8398
5	4·76	2451	22·4862	1·8346
10	9·09	2516	23·0825	1·8120
12·5	11·11	2548	23·3761	1·7976
15	13·04	2587	23.7340	1·7800
17·5	14·89	2591	23·7706	
18·36 .. 1 eq. HO	15·13	2466	22·6238	1·7590
20	16·66	2398	22·0000	1·7473
30	23·07	1523	13·9724	1·6700
36·73 .. 2 eqs. HO	26·86	1189	10·9090	1·6335
40	28·50	1056	9 6880	1·6146
50	33·33	810	7·4302	1·5600
60	37·50	626	5·7431	1·5118
70	41·17	535	4·9082	
80	44·44	450	4·1284	
100	50·00	382	3·5045	
120	54·54	332	3·0458	
140	58·33	290	2·6605	
160	61·53	260	2·3889	
180	64·28	241	2·2110	
200	66·66	227	2·0825	

The transpiration of sulphuric acid is very slow, being-twenty-four times less rapid than that of water, as might be expected from the viscous quality of the acid fluid. It is surprising, however, that the first additions of water do not promote the transpiration, although they lessen in a sensible degree the viscosity of the liquid. The transpiration-time increases from 2,360 to 2,591 seconds, and then attains the maximum, when 17·5 parts of water have been added to 100 parts of oil of vitriol. The proportion of water named approaches closely to one equivalent (18·36 parts). Indeed it is quite possible that the acid mixture which exhibits the least transpirability might have contained a full equivalent of water, for a portion of aqueous vapour may have been absorbed from the air during the process of filling the bulb. That the crystallisable hydrate of sulphuric acid, $SHO_4 + HO$, is the liquid

of least transpirability is, I believe, the proper inference from these observations. With increasing proportions of water, the transpiration-time rapidly diminishes, till the time is reduced to 227 seconds in a mixture of oil of vitriol with twice its weight of water.

A more minute examination than has been attempted would be required to show whether the existence of other definite hydrates of sulphuric acid may be indicated by a perceptible retardation in the time of transpiration.

Acetic Acid.

TABLE III.—Transpiration of Acetic Acid, at 20°, by Capillary C.

(Transpiration-time of water, 348 seconds.)

Water added to 100 acid ($C_4H_4O_4$).	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
0·8	0·8	445·5	1·2801	
15.. 1 eq. HO	13·04	890	2·5574	1·0735
20	16·66	921·5	2·6480	1·0742
25	20·00	931	2·6753	
27·5	21·56	933	2·6810	
30.. 2 eqs. HO	23·07	941	2·7040	1·0752
32·5	24·52	934	2·6839	1·0746
35	25·92	928	2·6666	
40	28·50	912	2·6207	
45	31·04	895	2·5718	
50	33·33	882	2·5344	1·0720
60.. 4 eqs. HO	37·50	852	2·4482	1·0700
90.. 6 eqs. HO	47·36	769	2·2098	

The glacial acetic acid made use of in these experiments still retained 0·8 per cent. of water. Its transpiration-time was 445·5 seconds. With the addition of 1 equivalent of water, the time rose to 890 seconds; and with 2 equivalents of water, to 941 seconds, when it attained its maximum. This last is the characteristic hydrate of acetic acid, $C_4H_4O_4 + 2HO$. It is marked out with great precision in these transpiration experiments. The times rise very gradually on either side, and appear to culminate exactly at that point. It is also the compound of water and acetic acid of maximum density, as is well-known. The transpiration-time of the hydrate referred to is so much as 2·7 times longer than that

of pure water. With 6 equivalents of water, acetic acid is still transpired 2·2 times more slowly than water.

Butyric Acid.

TABLE IV.—Transpiration of Butyric Acid, $C_8H_8O_4$, at 20°, by Capillary C shortened.

Transpiration-time of water, 290 seconds.)

Water added to 100 acid ($C_8H_8O_4$).	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
0	0	454	1·565	·9740
10·22 .. 1 eq. HO	9·27	828	2·855	·9901
20·45 .. 2 eqs. HO	16 98	951	3·279	·9975
30·67 .. 3 eqs. HO	23·47	969	3·341	
38·69 .. 4·8 eqs. HO	27·85	863	2·975	

In transpirability of its hydrates, burytic acid presents a considerable analogy to acetic acid, as might be expected from the rotation of these acids in composition. The time of the acid ($C_8H_8O_4$) is 1·565, referred to that of water as 1, and it rises to 2·855 by the addition of 1 equivalent of water. By a second equivalent of water, the time is increased to 3·279. Here, however, the progression does not immediately turn, as with acetic acid, but the time rises to 3·341 with 3 equivalents of water. With 3·8 equivalents of water the time is 2·975, and has accordingly very sensibly receded, the maximum point being passed. It is conceivable that the relation to acetic acid is slightly modified in butyric acid by the interference of some other physical property, such as unctuosity, that is unequally developed in the two acids.

Valerianic Acid.

The hydration of this acid cannot be carried beyond 2 equivalents, but up to that point the transpiration is retarded by every addition of water, as in acetic and butyric acids. While the basic hydrate ($C_{10}H_{10}O_4$) is transpired in 2·155 times the water period, the time increases to 3·634 with 1 equivalent of water added, and to 3·839 with 2 equivalents.

TABLE V.—Transpiration of Valerianic Acid, at 20°C, by Capillary C shortened.

(Transpiration-time of water, 290 seconds.)

Water added to 100 acid ($C_{10}H_{10}O_4$).	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
0	0	625·2	2·155	·9350
8·82 .. 1 eq. HO	8·10	1054	3·634	·9484
17·64 .. 2 eq. HO	15·84	1113·5	3·839	·9519

Formic Acid.

Formic acid appears to diverge considerably from the other members of the acetic acid series in certain physical and chemical characters. While the acetic hydrate is lighter than water, and is increased in density by the addition of water, the formic hydrate has a higher density than water, and has its density uniformly lowered by dilution, as will be seen in the Table which follows. The transpiration-time of formic acid, in a concentrated state, is also highest, and diminishes with dilution in the same regular manner as the density, showing no evidence of the acetic maximum at the point of 2 equivalents of water. Indeed, formic acid does not appear to affect that particular degree of hydration so characteristic of the acetic acid series. Hence it is, also, that we have no subformate of lead corresponding with the subacetate of lead, and have occasion to remark a general absence of basic formates. The physical properties of liquid formic acid are more suggestive of hydrochloric acid than they are of acetic acid.

The most concentrated formic acid that could be prepared still contained 3·6 per cent. of water. The transpiration-time of that liquid, it will be seen, is 1·718 referred to water as 1; and of the 2-hydrate 1·486. There is evidence of retardation between the points of 3 and 4 equivalents of water, but it is difficult to say with which of these two hydrates the retardation should be connected. More numerous and minute observations would be required to settle the point. We can only draw the negative conclusion from the Table, that the maximum retardation does not coincide with the 2-hydrate as in acetic acid.

TABLE VI.—Transpiration of Formic Acid, at 20°, by Capillary C shortened.

(Transpiration-time of water, 293 seconds.)

Water added to 100 acid ($C_2H_2O_4$).	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
3·73	3·6	503·5	1·718	1·2265
19·56 .. 1 eq.	16·35	484·5	1·653	1·2019
39·13 .. 2 eqs.	20·93	435·5	1·486	1·1765
58·69 .. 3 eqs.	36·98	411	1·402	1·1524
68·47 .. 3·5 eqs.	40·64	401·5	1·368	1·1466
78·26 .. 4 eqs.	43·90	402·5	1·372	1·1408
97·82 .. 5 eqs.	49·44	388·5	1·325	1·1275
117·35 .. 6 eqs.	53·99	376·5	1·284	1·1203
136·95 .. 7 eqs.	57·79	359	1·225	1·1062

Hydrochloric Acid.

The most concentrated form of this acid that was dealt with, acid of sp. gr. 1·1553, contained already upwards of 8 equivalents of water. Its transpiration-time was 1·736, referred to the time of water as 1. With further dilution, the time diminished, till at the proportion of 12 equivalents of water the time had fallen to 1·5287. About this point, the rate of diminution is reduced, and the transpiration-time even becomes stationary for a short portion of the range of hydration. The retardation observed appears to coincide with the formation of a 12-hydrate of hydrochloric acid. The existence of such a compound is further supported by the fact that solutions of hydrochloric acid tend to the same composition by evaporation at the atmospheric temperature. The degree of hydration of most stability at high temperatures, and having the highest boiling-point, is known to be at or near the proportion of the 16-hydrate. The existence, however, of the latter hydrate, at the ordinary temperature, is not supported by the transpiration experiments now recorded, conducted as these were at a low temperature.

TABLE VII.—Transpiration of Hydrochloric Acid, at 20°, by Capillary C.

(Transpiration-time of water, 348 seconds.)

Water added to 100 acid (HCl).	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
221·8	69·23	604	1·7356	1·1553
250	71·42	569	1·6336	1·1411
280	73·67	536	1·5404	1·1303
290	74·36	532	1·5287	
295·89 .. 12 eqs. HO	74·74	532	1·5287	1·1246
300	75·00	520	1·4942	
310	75·60	516	1·4827	1·1202
380	79 20	486	1·3965	1·1021
394 .. 16 eqs. HC	79·97	479	1·3764	1·0992
310	80·39	469	1·3476	1·0961

Alcohol.

The fundamental discovery made by Poiseuille of a point of maximum retardation in the transpiration of diluted alcohol is fully confirmed in the following series of observations. The transpiration-time rises from that of absolute alcohol, 1·1957 (water being 1), to 2·7872, when the alcohol is united with 6 equivalents of water, and then falls off again by further additions of water.

TABLE VIII.—Transpiration of Alcohol, at 20°, by Capillary D.

(Transpiration-time of water, 470 seconds.)

Water added to 100 Alcohol.	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
0	0	562	1·1957	
1	0·99	578	1·2297	·7069
3	2·91	615	1·3085	·8030
5	4·76	650	1·3829	·8083
7	6·54	695	1·4787	
10	9·09	734	1·5617	
20	16·66	851	1·8106	·8396
30	23·07	950	2·0212	·8557

TABLE VIII.—continued—

Water added to 100 Alcohol.	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
40	28·50	1029	2·1893	·8683
50	33·33	1093	2·3253	·8800
60	37·50	1152	2·4510	·8897
70	41·17	1213	2·5808	·8983
72·5	42·02	1230	2·6170	·9003
75	42·85	1231	2·6191	·9021
78·26 .. 4 eqs. HO	43·94	1239	2·6361	·9045
80	44·44	1238	2·6340	·9058
82·5	45·20	1242	2·6425	·9073
85	45·94	1244	2·6468	·9088
90	47·36	1256	2·6723	·9120
100	50·00	1268	2·6978	·9183
110	52·38	1282	2·7276	·9235
112·5	52·94	1287	2·7382	·9249
115	53·49	1298	2·7617	·9255
117·39 .. 6 eqs. HO	54·04	1310	2·7872	·9271
120	54·54	1307	2·7808	·9288
122	55·05	1300	2·7659	·9292
125	55·55	1297	2·7595	·9304
130	56·52	1297	2·7595	·9328
140	58·33	1295	2·7553	·9363
150	60·00	1280	2·7234	·9396
160	61·53	1255	2·6702	·9430
170	62·92	1250	2·6505	·9451
180	64·28	1246	2·6510	·9482
190	65·51	1240	2·6382	·9500
200	66·66	1235	2·6276	·9521
250	71·42	1165	2·4787	·9601
300	75·00	1094	2·3276	·9652
350	77·77	1026	2·1829	·9689
400	80·00	973	2·0702	·9716
450	81·80	934	1·9872	·9738
500	83·33	908	1·9319	·9759

It will be observed that, after attaining its maximum, the transpiration-time falls off in a very gradual manner, till at least another equivalent of water has been added. With still further dilution, the shortening of the transpiration-time is considerably more rapid. The Table appears to indicate a slight retardation at the proportion of four equivalents of water; but this would require confirmation. It is remarkable that hydrated liquid compounds appear in general to show only one decided transpiration maximum, as with the 1-hydrate in sulphuric acid, the 2-hydrate in acetic acid, the 3-hydrate in nitric acid, the 6-hydrate in alcohol, and the 12-hydrate in hydrochloric acid.

A considerable number of experiments were made upon specimens of *methylic alcohol* prepared at different times, with some discrepancy in the results. Although always derived from crystallized methylic oxalic ether, the liquid varied sensibly in transpirability. As the cause of this variation has not yet been ascertained, I shall confine myself at present to one statement, namely, that a particular specimen of methylic alcohol gave 0·63 as the transpiration-time of the anhydrous substance (water being 1), and 1·8021 as the time of the 6-hydrate, $C_2H_4O_2 + 6HO$, and that for a considerable distance on either side of that point of hydration, the transpiration was slightly less and nearly constant, as it is in vinic alcohol. It may be inferred, therefore, with some probability, that alcohols have a maximum of retardation at the same stage of dilution.

Three alcohols in a state of purity were transpired through the same capillary, with water for comparison, at 20°. The time of water was 297 seconds.

TABLE IX.—Transpiration of Alcohols, at 20°.

	Transpiration-time.		Spec. grav. at 15°.	Boiling-point.
	In seconds.	Water = 1.		
Methylic alcohol	187·25	0·630	·7973	66° C.
Vinic alcohol	355·1	1·195	·7947	78·5
Amylic alcohol	1084	3·649	·8204	132

It will be remarked that the transpiration-time of an alcohol increases with the elevation of its temperature of ebullition. A similar observation applies to the transpiration of ethers.

TABLE X.—Transpiration of Ethers, at 20°, by Capillary C shortened. (Transpiration-time of water, 290 seconds.)

	Transpiration-time.		Spec. grav. at 15°.	Boiling-point.
	In seconds.	Water = 1.		
Formate of ethyl	148·2	0·511	·9174	55°·5
Acetate of ethyl	160·5	0·553	·8853	74
Butyrate of ethyl	217·5	0·750	·8490	114
Valerate of ethyl	237·5	0·827	·8750	133·5

The transpiration-times of the homologous acids, previously observed, appear also to follow in progression.

Transpiration of Acids, at 20°.

	Acid.	Acid + 2HO.
Acetic acid	1·2801	2·740
Butyric acid	1·565	3·279
Valerianic acid	2·155	3·839

The increase of the transpiration-time of an alcohol, ether, and acid, as each rises in its series, may be connected with the increasing weight of their molecule.

Acetone.

The transpiration of this liquid is remarkably rapid. It is also greatly retarded by the addition of water. The time will be found to rise from 0·401, that of anhydrous acetone, to 1·604, the time of the 12-hydrate, taking the equivalent of acetone as $C_6H_6O_2$, or of the 6-hydrate with the equivalent C_3H_3O.

TABLE XI.—Transpiration of Acetone, at 20°, by Capillary C. (Transpiration-time of water, 348 seconds.)

Water added to 100 acetone ($C_6H_6O_2$).	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
0	0	139·6	0·401	·7943
15·51 .. 1 eq.	13·42	212·5	0·610	·8384
31·03 .. 2 eqs.	23·68	283·5	0·814	·8604
46·55 .. 3 „	31·76	355·5	1·021	·8850
62·06 .. 4 „	38·29	457	1·313	·8990
77·58 .. 5 „	43·68	464	1·333	·9123
85·34 .. 5·5 „	46 04	469	1·347	·9173
93·10 .. 6 „	48·21	482	1·385	·9219
100	50·00	500	1·436	·9251
108·61 .. 7 „	52·06	515·5	1·479	·9300
124·13 .. 8 „	55·33	531·5	1·527	·9320
139·65 .. 9 „	57·85	537·7	1·543	·9413
155·16 .. 10 „	60·81	552·7	1·586	·9468
170·67 .. 11 „	63·05	555·5	1·594	·9504
186·18 .. 12 „	65·05	558·5	1·604	·9526
201·71 .. 13 „	66·85	556·5	1·599	·9563
217·24 .. 14 „	68·41	557	1·600	·9588
232·75 .. 15 „	69·94	553·5	1·590	·9608
248·27 .. 16 „	71·28	549	1·577	·9632
263·79 .. 17 „	72·23	547	1 571	·9649
279·31 .. 18 „	73·63	546	1·568	·9662
294·82 .. 19 „	74·67	539·5	1·550	·9676
372·24 .. 24 „	78·82	519	1·491	·9736

The transpiration-time of acetone attains a maximum at what is represented in the Table as the compound with 12 equivalents of water. The time is nearly stationary for some distance on either side of that point, the range from 10 to 15 equivalents of water being 1·586 to 1·590, with 1·604 as a maximum for the intermediate twelfth equivalent.

Glycerin.

This liquid is too viscid in a state of purity to be transpired by means of the bulb and capillaries employed in these experiments. The observations to be recorded were confined to diluted solutions of glycerin approaching in composition to the 18-hydrate, $C_8H_8O_6 + 18HO$. It was imagined that glycerin, as a triatomic alcohol, might affect combination with water in the proportion named.

TABLE XII.—Transpiration of Glycerin, at 20°, by Capillary C.

(Transpiration-time of water at the same temperature, 348 seconds.)

Water added to 100 Glycerin ($C_6H_8O_6$).	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
170	62·96	1190	3·445	1·1010
176·07.. 18 eqs.	63·77	1160	3·333	1·0980
180	64·28	1131·5	3·251	1·0960
190	65·51	1068·5	3·070	1·0934
192	65·75	1054	3·031	1·0927
195	66·10	1049	3·014	1·0914
197	66·32	1039	2 977	1·0912
200	66·66	1026	2·948	1·0905

The transpiration-time of the 18-hydrate is 3·333, referred to water as 1. There is no indication of a maximum at that point, but the numbers descend according to their place in the Table without any interruption.

The idea having suggested itself that the viscous property of glycerin-solutions might overpower or conceal the expected deviation, the transpiration was repeated at a higher temperature, when the solutions possess greater fluidity.

TABLE XIII.—Transpiration of Glycerin, at 60°, by Capillary C.

(Transpiration-time of water at the same temperature, 186 seconds.)

Water added to 100 Glycerin ($C_6H_8O_6$).	Water, per cent.	Transpiration-time.		Spec. grav. at 15°.
		In seconds.	Water = 1.	
170	62·96	435·5	2·341	1·1010
172·5	63·30	432	2·322	1·0999
175	63·63	428	2·301	1·0980
176·08 .. 18 eqs.	63·77	425	2·284	1·0976
177	63·96	422·5	2·271	1·0970
180	64·22	420	2·258	1·0960

Still no retardation appears at the point of 18 equivalents, but the time continues to shorten as the proportion of water is increased, according to a pretty uniform progression. The information respecting the constitution of glycerin which transpiration affords is therefore of a negative character.

The existence of a relation between the transpirability of liquids and their chemical composition appears to be established. It is a relation analogous in character to that subsisting between the boiling-point and composition, so well defined by Hermann Kopp. Perhaps the most interesting part of the present subject to develop would be the transpiration of homologous series of substances. Judging from the limited observations on the alcohols, ethers, and acids, the order of succession of individual substances in any series would be indicated by the degree of transpirability of these substances, as clearly as it is by their comparative volatility. In carrying out the inquiry, it would probably be found advantageous to operate at a fixed and somewhat elevated temperature. A large number of substances are liquid at 100°, of which the transpiration-time could be easily obtained.

In hydrated substances, transpiration also affords a manifestation of definite combination at once striking and precise. I need only refer to the manner in which the "constitutional" hydrate of sulphuric acid SHO_4+HO, of acetic acid $C_4H_4O_4+2HO$, of nitric acid NHO_6+3HO, and of alcohol $C_4H_6O_2+6HO$ is each indicated by its maximum transpiration-time. The indication of the alcohol-hydrate is particularly distinct, although that hydrate

must be a comparatively feeble compound. Indeed the extent to which transpiration is affected by the annexation of constitutional water appears to be by no means in proportion to the intensity of combination.

The increased resistance to transpiration observed in these definite hydrates may be connected with their larger molecules. But another speculative view of the retardation can be suggested, in which the phenomenon is referred to a physical agency. When one of these definite hydrates, say the 6-hydrate of alcohol, is being forced through the capillary, it may be imagined that a small portion of the hydrated compound is molecularily decomposed by the friction. A certain portion of the impelling force would thereby be lost, being converted into the latent heat which alcohol and water require to assume when separated from each other, and the transpiration be consequently retarded; for as alcohol and water evolve heat on combining, so they must absorb heat when their union is dissolved by any cause. But the change of temperature representing the lost force appears to be too small to be rendered sensible to observation. It would be capable of raising the temperature of the transpired liquid not more than about one forty-third part of a degree, according to an accurate estimate for which I am indebted to Professor Stokes. In consequence of this circumstance, the physical hypothesis now suggested has neither been verified nor disproved.

To this paper are appended two series of observations made on transpiration at different temperatures, the first series being the transpiration of water, and the second that of absolute alcohol. Each series of experiments is repeated with two capillary tubes, one having nearly double the resistance of the other. The numbers from the two capillaries exhibit a fair amount of agreement. The times given are those actually observed, no correction being made for the small variation of the capillary in diameter at different temperatures.

The dimensions of Capillary D were as follows:—Capacity of bulb, 4·135 cub. cent.; length of capillary tube, 37·5 millims.; diameter of bore, 0·10325 millim. Time of passage of water, at 20°, under pressure of one atmosphere, 470 seconds.

The dimensions of Capillary E were as follows:—Capacity of bulb, 3·725 cub. cent.; length of capillary, 53 millims.; diameter of bore, 0·0858 millim. Time of passage of water, at 20°, under pressure of one atmosphere, 913 seconds.

TABLE XV.—Transpiration of Alcohol at different Temperatures.

Temperature.	By capillary tube D.					By capillary tube E.				
	Time in seconds.	Time and velocity of water at 20° = 1.		Time and velocity of water at 0° = 1.		Time in seconds.	Time and velocity of water at 20° = 1.		Time and velocity of water at 0° = 1.	
		Time.	Velocity.	Time.	Velocity.		Time.	Velocity.	Time.	Velocity.
°C.										
0	860	1·8297	0·5465	1·0238	0·9767	1642	1·7984	0·5560	1·0079	0·9920
1	840	1·7893	0·5588	1·0012	0·9988	1601	1·7535	0·5702	0·9828	1·0174
3	607	1·7170	0·5824	0·9607	1·0409	1537	1·6834	0·5940	0·9435	1·0598
5	772	1·6425	0·6089	0·9190	1·0880	1473	1·6134	0·6198	0·9042	1·1059
7	738	1·5702	0·6368	0·8785	1·1382	1410	1·5443	0·6475	0·8656	1·1553
10	700	1·4893	0·6714	0·8333	1·2000	1350	1·4786	0·6755	0·8226	1·2066
15	624	1·3276	0·7532	0·7428	1·3461	1213	1·3285	0·7526	0·7446	1·3429
20	562	1·1957	0·8362	0·6690	1·4946	1092	1·1960	0·8360	0·6703	1·4917
25	520	1·1063	0·9038	0·6190	1·6154	1001	1·0963	0·9120	0·6145	1·6273
30	476	1·0127	0·9873	0·5566	1·7646	915	1·0022	0·9978	0·5617	1·7803
35	428	0·9106	1·0981	0·5095	1·9626	843	0·9233	1·0830	0·5175	1·9323
40	391	0·8319	1·2020	0·4654	2·1483	772	0·8455	1·1826	0·4739	2·1101
45	360	0·7659	1·3055	0·4285	2·3333	707	0·7743	1·2913	0·4340	2·3041
50	331·5	0·7053	1·4177	0·3946	2·5339	645	0·7064	1·4155	0·3959	2·5100
55	307	0·6531	1·5309	0·3654	2·7301	592	0·6484	1·5422	0·3634	2·7517
60	285	0·6063	1·6491	0·3392	2·9373	551	0·6035	1·6569	0·3382	2·9564
65	262	0·5574	1·8005	0·3119	3·2061	510	0·5585	1·7901	0·3130	3·1941
70	241	0·5127	1·9502	0·2869	3·4854	468	0·5125	1·9465	0·2873	3·4807

TABLE XIV.—Transpiration of Water at different Temperatures.

TABLE XIV.—Transpiration of Water at different Temperatures.

Temperature.	By capillary tube D.					By capillary tube E.				
	Time in seconds.	Time and velocity of water at 20° = 1.		Time and velocity of water at 0° = 1.		Time in seconds.	Time and velocity of water at 20° = 1.		Time and velocity of water at 0° = 1.	
		Time.	Velocity.	Time.	Velocity.		Time.	Velocity.	Time.	Velocity.
°										
0	840	1·7872	0·5593	1·	1·	1629	1·7872	0·5604	1·	1·
1	792	1·6851	0·5934	0·9428	1·0606	1568	1·7174	0·5829	0·9625	1·0389
2	770·5	1·6391	0·6099	0·9172	1·	1514	1·6582	0·6050	0·9294	1·
3	749	1·5936	0·6275	0·8917	1·1216	1461	1·6002	0·6249	0·8975	1·1449
4	727	1·5468	0·6465	0·8654	1·					
5	709	1·5085	0·6629	0·8440	1·1857	1382	1·5136	0·6606	0·8483	1·1787
7	669	1·4234	0·7025	0·7964	1·2556	1289	1·4118	0·7083	0·7912	1·2638
10	618	1·3148	0·7605	0·7357	1·3592	1188	1·3012	0·7685	0·7293	1·3717
14	548	1·1659	0·8576	0·6423	1·5328					
15	533	1·1340	0·8818	0·6345	1·5759	1037	1·1358	0·8804	0·6366	1·5709
16	521	1·1085	0·9021	0·6202	1·6122					
20	470	1·	1·	0·5595	1·7872	913	1·	1·	0·5604	1·7842
25	414	0·8808	1·1352	0·4928	2·0189	823	0·9014	1·0904	0·5052	1·9793
30	375·5	0·7989	1·2516	0·4470	2·2371	743	0·8138	1·2288	0·4501	2·1924
35	338	0·7191	1·3905	0·4023	2·4852	670	0·7338	1·3626	0·4113	2·4313
40	309·5	0·6508	1·5185	0·3684	2·7108	602	0·6593	1·5166	0·3695	2·7059
45	284·5	0·6053	1·6520	0·3386	2·9525	553	0·6056	1·6509	0·3394	2·9459
50	261	0·5553	1·8007	0·3107	3·2184	505	0·5531	1·8079	0·3100	3·2257
55	243	0·5170	1·9341	0·2892	3·4979	475	0·5202	1·9221	0·2916	3·4294
60	228	0·4851	2·0614	0·2714	3·6842	438	0·4797	2·0844	0·2689	3·7191
65	214	0·4553	2·1967	0·2547	3·9252	400	0·4381	2·2825	0·2455	4·0725
70	200	0·4155	2·3500	0·2380	4·2000	378	0·4140	2·4153	0·2321	4 3122

LII.—*On the Chemistry of Opium.*

[A Discourse delivered to the Fellows of the Chemical Society, May 1st, 1862.]

By Thomas Anderson, M.D., F.R.S.E., Professor of Chemistry in the University of Glasgow.

The chemical history of opium may be said to have its origin so far back as the year 1803, when Desrone announced that he had extracted from it a peculiar crystalline substance, in which he believed its narcotic properties to reside. In a chemical point of view, his investigation was of minor importance, and it would scarcely merit notice, if it were not that it had an important influence in starting the idea which has proved so prolific in important results, that the therapeutic properties of medicinal substances depend upon the presence of particular active principles readily separable from the inert matters of which their bulk is composed. Desrone evaporated the aqueous solution of opium to a syrup, and, after allowing it to stand for some time, a gritty matter deposited, which was scarcely soluble in water, but crystallised easily from alcohol and ether. From his description of its properties it was obviously narcotine; but he did not observe its power of combining with acids, and his observations were far from definite, and did not attract much attention.

No one, indeed, appears to have followed them up until the year 1817, when Sertürner made the next step in the investigation of opium, and published the result of researches which had occupied him for several years. He detected meconic acid and morphia, but curiously enough failed to obtain Desrone's substance, which he therefore supposed to have been a meconate of morphia.

A considerable time again elapsed without any further progress being made; but in 1826 Dublanc discovered meconine, and described its properties very distinctly, although he did not give it a name—an omission supplied by Couerbe in 1830. During the several years following the latter date, opium was subjected to a very minute investigation by Couerbe, Pelletier, Robiquet, Merck, and others, who added codeine, thebaine, narceine, and porphyroxine to the list of its crystalline constituents. Subsequently to their time, little was done except to add a few

analyses of the substances discovered by these observers, but without extending in any marked degree our knowledge of their chemical relations, until 1844, when Wöhler and Blyth separately examined narcotine, and made it the starting point of a very remarkable series of products.

In the year 1850 I was myself induced to commence the study of some of the principles of opium; and at that time I found our knowledge sufficiently extensive, but greatly deficient in precision. The constitution of meconic acid, morphia, and narcotine appeared sufficiently established; that of codeine was expressed by several different formulæ, of which, one recently proposed by Gerhardt had probability in its favour, and was fully confirmed by my own researches; but all that was known regarding the other subtances was in the last degree unsatisfactory, and based on the imperfect and often conflicting statements of their discoverers, and on analyses made at a time when the methods in use were deficient in that accuracy and precision which they have since attained. It was obvious indeed that the whole subject required revision, and I made it my task to do this in the first instance; but I was naturally led to extend my investigation to the study of the products of decomposition of the different substances, so far as the amount of material at my disposal permitted, and I am still engaged with the subject.

The mass of facts which has now been accumulated regarding the chemistry of opium renders it necessary for me to discuss it very succinctly here, and without entering into details. I pass altogether without mention its indeterminate constituents, although many curious observations have been made in relation to them, and proceed at once to the crystalline substances of which no fewer than twelve—nine well-determined and three doubtful—have been described. They are—

Morphine.	Thebaine.	Porphyroxine?
Codeine.	Narceine.	Opianine?
Papaverine.	Meconine.	Meconic acid.
Narcotine.	Pseudomorphine?	Thebolactic acid.

A critical review of the processes employed for the preparation of these substances would be of much interest, though by no means suited to the present occasion. It is very obvious that the results obtained by different experimenters have greatly depended on the methods they have pursued. We observe that one individual obtains

particular substances abundantly, another only in very small quantity, and the difference is often due to modifications in the mode of working, which, at first sight, appear very trifling. Even the quantity of water employed in the primary solution of the opium is important, and greatly affects the quantity of resinoïd matters dissolved, and, by consequence, the facility with which some of the bases are made to separate in the crystalline form. Thus I have found narceine very abundantly, while other observers obtain it in small quantity, and have altogether failed to detect pseudomorphine and porphyroxine, although I have sought for them with some care; nor have I noticed thebolactic acid, which the Messrs. Smith state they separate in large quantity. It is true that my attention has not been directed to the acids of opium; but had the substance in question been easily obtainable in the course of the process I have followed, it could scarcely have been overlooked. The investigator of opium is placed at a certain disadvantage by the necessity of making use of the refuse of the manufacture of morphine by processes in which everything is sacrificed to obtaining the maximum quantity of that alkaloid, irrespective of the others associated with it, and for the preparation of which it by no means follows that they are equally advantageous, and it can scarcely be doubted that, if it were possible to operate on a hundred weight or two of opium by methods entirely different from those now in use, results of much interest might be obtained.

For the preparation of morphine, the process originally proposed by Robertson and Gregory, has, in this country at least, proved itself the most suitable, and in skilful hands, is found to yield a larger proportion of the base than any other. It is so well known, that it is hardly necessary to refer to it here, the more especially as, so far as I know, no change has taken place in the principle on which it is founded, although, of course, there is abundant scope for judgment and skill in carrying out the manipulative details. The principle involved is very simple. The bases are present in opium chiefly as meconates, which are difficultly crystallisable salts; but on the addition of chloride of calcium, meconate of lime precipitates, and the chlorides remain in the solution, of which the hydrochlorates of morphine and codeine are readily crystallisable, and separate from the concentrated solution, leaving the other bases behind in the mother-liquor. It is from the residue left, after

complete separation of the morphine, that I have extracted the bases I examined, and the process I have found most convenient is the following:—

The mother-liquor, which has the consistence of treacle, and is perfectly black, is diluted with water, and ammonia added. An abundant dark-brown precipitate falls, consisting of narcotine, papaverine, and thebaine, accompanied, as I have recently observed, by a small quantity of codeine, the presence of which could scarcely have been expected, and all contaminated with a brown resinous substance. This precipitate, which is at first quite granular, runs together into a resinous mass, if allowed to lie in the fluid, and the mother-liquor is thus squeezed out of it as effectually as if it were put into a powerful press. By solution of this precipitate in boiling spirit, impure crystals of narcotine are obtained on cooling, which may be purified by animal charcoal and successive crystallisations. By distilling down the solution, a further crop of crystals is dissolved, and finally a dark mother-liquor is obtained, from which *thebaine* and *papaverine* may be prepared. For this purpose water is added; the liquid is rendered slightly acid by acetic acid; and the resin which is thus separated is filtered off; subacetate of lead is then added to the filtrate until it restores the blue of reddened litmus; and the precipitate being separated, the excess of lead is removed by sulphuretted hydrogen, or more conveniently by sulphuric acid. Ammonia then precipitates the thebaine, still contaminated with resinous matters, from which it is separated by crystallisation from absolute alcohol, and decolorised by animal charcoal. Papaverine may be extracted from the lead-precipitate by digesting it with alcohol, evaporating the liquid, treating it with hydrochloric acid, filtering from resin, concentrating, and leaving the solution to itself for some time, when the sparingly soluble hydrochlorate of papaverine slowly crystallises. Precipitation with ammonia and crystallisation from spirit, give the base itself in a state of purity.

The mother-liquor from which the precipitate of these bases has been separated, contains *narceine* and *meconine*, with a small quantity of papaverine. On concentrating it, narceine separates in abundance, and is easily obtained pure by washing with a small quantity of cold water, and crystallisating two or three times. It is remarkably distinguished by the facility with which it is obtained free of colour, for which purpose animal charcoal is not required.

After concentrating the liquid, until the narceine is separated, the residue is agitated with ether, which extracts meconine, together with a little papaverine.

Meconic acid is prepared from the meconate of lime, obtained in the first part of Robertson and Gregory's process, according to a method well-known. Of the preparation of thebolactic acid, no description has yet been published.

Morphine, by far the most important of the constituents of opium, is as yet but imperfectly examined. Its constitution, long expressed in chemical works by the formula $C_{35}H_{20}NO_5$; this formula was altered by Gerhardt to $C_{34}H_{19}NO_6$, which has been universally adopted, and confirmed by subsequent researches. Little is known regarding the products of its decomposition; but the researches of How have shown that it belongs, like most of the other natural alkaloids, to the group of nitril bases. It exists in opium to the extent of about 10 or 12 per cent., but the proportion differs greatly in different varieties, being largest in opium produced from the poppy grown in this country, which is said to have yielded as much as 20 per cent., while in East India and in Egyptian opium it often does not exceed 5 or 6 per cent. Turkey opium is that from which it is most commonly extracted, but even then its quality varies very greatly; and as the amount contained in different specimens is a matter of much importance to the manufacturer, various attempts have been made to devise a method by which the amount contained in a given sample might be quickly and accurately ascertained. Mohr and other chemists have given processes for this purpose; but none of them have proved trustworthy, the fact being that the conditions under which morphine is completely separated, differ for every sample, and the manufacturer finds it much safer to rely upon his eye, which enables an experienced observer to form an opinion which, if not always correct, is safer than any chemical process.

The introduction of Robertson and Gregory's process led to the discovery of *codeine*, Robiquet having observed that when the morphine was precipitated from the muriate obtained by it, another base remained in solution along with the sal-ammoniac formed. His idea was that the liquid contained a double salt of codeine and ammonia. But I have satisfied myself that this view is erroneous, having obtained pure hydrochlorate of codeine from the liquid by crystallisation alone.

The earlier analyses of codeine led to the conclusion that it

differed from morphine by a single equivalent of oxygen, and it was represented by the formula $C_{35}H_{20}NO_6$, which was called in question by Gerhardt. He made two analyses of the hydrated base, and obtained results corresponding with $C_{36}H_{21}NO_6$, which I have fully confirmed. Codeine, therefore, so far as its constitution is concerned, may be considered as a homologue of morphine, but they present none of that similarity in properties which is usually so conspicuous in the adjacent members of a homologous series. Nothing, indeed, can be more marked than the difference between morphine, insoluble in water and ether, and but sparingly dissolved by alcohol, and codeine, which is readily and abundantly taken up by all these menstrua. Other differences also exist, which render it very questionable whether the two bases can be considered as homologous. Codeine yields many beautiful substitution-products, which are obtained with some difficulty. I have described nitro-codeine $C_{36}H_{20}(NO_4)NO_6$, chlorocodeine $C_{36}H_{20}ClNO_6$, and bromocodeine $C_{36}H_{20}BrNO_6$, all obtained by the cautious action of the different substances on the base itself, and remarkably definite compounds. Indications of an iodine substitution-compound were also obtained; but the most remarkable iodine-compound is that which I have called teriodocodeine, without intending thereby to define its chemical nature. It contains the elements of one equivalent of codeine and three equivalents of iodine, and belongs to a class of compounds of whose rational constitution we have no definite ideas. It is obtained in beautiful doubly oblique crystals, displaying the phenomena of pleochroism in a very striking manner.

Thebaine was discovered by Pelletier in 1832, and described by him under the name of paramorphine, his analysis having led to the conclusion that it was isomeric with morphine; the inaccuracy of this opinion was shown by Couerbe and Kane, although neither of them succeeded in fixing its true constitution. My own analyses show that it contains $C_{38}H_{21}NO_6$, thus differing from codeine by two equivalents of carbon. It is quite insoluble in water, but extremely soluble in alcohol and ether, from the former of which it is deposited in tabular crystals on cooling. Strong sulphuric acid produces with it a deep red colour. When diluted, the acid dissolves it, and on standing for some time, a resinous substance deposits, which, on treatment with boiling water, dissolves, and on cooling, gives sparingly soluble crystals. Its salts crystallise well. Of its decomposition-products, nothing

is yet known, but as I have now obtained a larger quantity of the base, I trust I may, at no distant date, be enabled to supply some information on this point.

Papaverine.—This base was discovered by G. Merck in 1850, and was obtained from an old opium residue. It appears, however, to be an invariable constituent of opium, and in not inconsiderable quantity. It is obtained in small needles, generally grouped in radiated masses, highly soluble in boiling alcohol and distinguished from the other opium-bases by giving a fine blue with concentrated sulphuric acid. Its salts crystallise well, the hydrochlorate more particularly being obtained in fine crystals. Its formula is $C_{40}H_{21}NO_8$. One of its most singular peculiarities is its tendency to carry down with it ammonia, when precipitated by that base; both Merck and myself obtained in its analysis a quantity of nitrogen considerably in excess of the theoretical quantity, and it was only by precipitating with potash, that I succeeded in obtaining an accurate result. It yields several well-marked substitution products, among which, nitropapaverine, which crystallises in pale buff needles, and yields sparingly soluble salts, and bromopapaverine, are the most characteristic.

Narceine is distinguished from all the other opium-bases by its solubility in water, whence it crystallises in fine silky needles, which are deposited in such abundance that a solution saturated at the boiling point becomes nearly solid on cooling. Its basic properties are very feeble, so much so indeed, that both Pelletier, its discoverer, and Couerbe who afterwards examined it, maintain, that it is incapable of combining with acids; but in this respect they were in error, for it gives well-marked salts. Its formula is $C_{46}H_{29}NO_{18}$. Its decompositions are as yet unknown, but I have observed that it is capable of producing certain substitution-products, and also of undergoing further changes, which I intend to investigate further.

Narcotine is by far the most interesting and remarkable of the opium-bases. Indeed, its remarkable decompositions, and the number of highly crystalline products it yields, give it claims to be considered as the most interesting of the natural alkaloids. Although discovered by Desrone at the beginning of the present century, its chemical history may be said to date from the year 1844, when Wöhler and Blyth separately obtained some of its most important decomposition-products. Wöhler found that, when treated with oxide of manganese and sulphuric acid, it yielded a new base and acid, which he called *cotarnine* and

opianic acid. Blyth, in endeavouring to determine the constitution of narcotine by the analysis of its platinum-salt, observed that an excess of bichloride of platinum produced the same decomposition. His investigation led him to the conclusion that its formula was $C_{46}H_{25}NO_{14}$, which afforded a sufficient explanation of the results obtained by Wöhler and himself, and also harmonized with the researches I made at a subsequent period. More recently, Messrs. Matthiessen and Foster have again revised the formula of narcotine, and give $C_{44}H_{23}NO_{14}$ as the nearest expression of their results, and as likewise affording an easy explanation of its products of decomposition. It is not possible, in the present state of our knowledge, to decide positively between these two formulæ, and a similar uncertainty exists as to that of cotarnine, for which Blyth's analyses give $C_{26}H_{13}NO_6$, and those of Matthiessen and Foster $C_{24}H_{13}NO_6$; but there is no doubt as to the constitution of the non-nitrogenous substances produced along with it. Wöhler and Blyth obtained only opianic and hemipinic acids by treating narcotine; but by using nitric acid, I obtained, in addition, another substance which proved to be meconine, a base long before obtained by Couerbe, existing ready formed in opium, and having the formula $C_{20}H_{10}O_8$. Opianic and hemipinic acids, which are simultaneously produced, may be considered as higher degrees of oxidation of this substance, being respectively $C_{20}H_{10}O_{10}$ and $C_{20}H_{10}O_{12}$. The explanation of the decomposition of narcotine by oxidising agents must differ according as we accept the formulæ of Blyth, or those of Matthiessen and Foster. According to the former, narcotine may be represented as if it were a compound of meconine and cotarnine, plus hydrogen. Thus—

$$C_{46}H_{25}NO_{14} = C_{20}H_{10}O_8 + H_2 + C_{26}H_{13}NO_6,$$

and the action consists in the oxidation of two equivalents of hydrogen, while the further addition of two or four equivalents of oxygen would produce opianic or hemipinic acid. According to the latter view, narcotine would be simply a compound of meconine and cotarnine, thus—

$$C_{44}H_{23}NO_{14} = C_{20}H_{10}O_8 + C_{24}H_{13}NO_6,$$

and in that case the formation of opianic and hemipinic acids would be due to the direct addition of O_2 or O_4, while the breaking up into meconine and cotarnine must be explained upon

a different principle. An experiment made by me long since, and to which reference is made at the close of one of my papers,* may serve to throw some light on this point. I exposed narcotine along with a slight excess of sulphuric acid, to a heat of 280° F., in a sealed tube, and thus obtained sulphate of cotarnine and meconine, and we may suppose that when the latter substance is obtained by the action of nitric acid, the change in both cases may be due to the strong acid simply expelling the meconine from its combination with cotarnine. It is fair to say, however, that the action is not so simple as here represented, and I invariably found that a dark-coloured substance was produced at the same time, the properties of which I have not yet examined.

Meconine or opianyl, as I prefer to call it, opianic and hemipinic acids, as well as cotarnine, are capable of yielding an extensive series of products of the most interesting kind, the relations of which are, however, far from being as yet completely worked out, and the discussion of whose properties would carry us far beyond the limits of the present paper. It is impossible, however, to avoid mentioning the facility with which they all yield methyl-compounds. Thus narcotine, when treated with hydriodic acid, gives 3 equivalents of iodide of methyl, and cotarnine and its products give methylamine with great ease. This is particularly the case with apophyllic acid, which, when boiled with excess of potash, evolves it readily, and an acid free from nitrogen is obtained. Apophyllic acid, which is formed by the action of nitric acid on cotarnine, is $C_{16}H_7NO_8$, and my observations lead me to suppose that it is a methylamic acid; should further investigations establish this, it would be represented by the formula $C_{14}H_2(C_2H_5N)O_8$, and contain an acid, $C_{14}H_4O_{10}$, which must bear a near relation to meconic acid, thus—

Supposed new acid	$C_{14}H_4O_{10}$
Meconic acid	$C_{12}H_4O_{10}$

Some years since Wertheim announced that he had ascertained the existence of three different kinds of narcotine in opium, which he called methylo-, ethylo-, and propylo-narcotine. These substances, however, I have been unable to detect, although a considerable number of different specimens of narcotine have passed through my hands; and as Messrs. Matthiessen and

* Edinburgh Philosophical Transactions, vol. xxi., part i.

Foster have come to the same conclusion, little doubt can be entertained that Wertheim's idea is erroneous.

It will scarcely be necessary for me to refer at length to the three doubtful constituents of opium, except to say that they require further investigation. I must observe, however, that although I have followed, as nearly as circumstances would permit, the process given for their preparation, I have failed to detect the slightest indication of them; and it is probable that they are met with only in particular kinds of opium and in exceptional circumstances. This is certainly the case with opianine, which Hinterberger states he found in Egyptian opium, and in regard to which his statements are very imperfect. He originally gave for it the formula $C_{66}H_{36}NO_{23}$, which he afterwards altered to $C_{66}H_{36}N_2O_{21}$, but in neither case is there any satisfactory evidence of the accuracy of the results. Still less can be said for the formula $C_{27}H_{18}NO_{24}$ assigned to pseudomorphine, and as to porphyroxine nothing is known.

It has often been a matter of discussion whether these substances, which have been obtained from opium, are to be considered as educts or as products, that is, whether they pre-exist in it, or are the result of decompositions occurring during the process of extraction. As a chemical question, it would, of course, be most interesting to ascertain that they were products. The discovery of the decomposition of narcotine, with the production of meconine, may be taken as pretty conclusive evidence that it at least is a product; and if so, it may be fairly inferred that cotarnine must exist in the opium, although it has not been detected therein. Those, however, who are best acquainted with the properties of that base, will best understand the difficulty which besets its separation from such a substance a opium, and will not be inclined to doubt that it must exist there.

As regards all the other constituents of opium, they must be considered as educts, for notwithstanding a tolerably close connection between the *formulæ* of some of them, there is no evidence as to any relationship in constitution. We speak, however, on this point in ignorance; for what has now been said, is sufficient to show that, notwithstanding the mass of facts accumulated, our knowledge of many of the opium constituents is far from perfect, and that there is abundant scope for further investigation.

LIII.—*On the Constitution of Melampyrin.*

By Dr. Erlenmeyer and J. A. Wanklyn, Esq.

In our paper on Mannite* we remarked that, notwithstanding the abundance of that substance, and the labour which had been bestowed upon its investigation, chemists were by no means sure of its formula. We showed further that, by subjecting that body to the action of hydriodic acid, iodide of hexyl was formed; and thus we established the formula which is in general use.

But if a degree of doubt existed as to the real composition of mannite, what shall we say about the composition of the rare members of the mannite family, some of which, obtained in small quantities from rare plants, have been investigated only by their discoverers.

In a recent paper, bearing the title "On the identity of Melampyrin with Dulcit,"† Gilmer has pointed out, very strikingly, one of the peculiar difficulties which beset the investigation of this class of compounds. Gilmer analysed melampyrin, and then found that there were three probable formulæ, which expressed his analysis:—

	$C_5H_{12}O_5$	$C_6H_{14}O_6$	$C_7H_{16}O_7$
C	39·47	39·56	39·62
H	7·90	7·70	7·55
O	52·63	52·74	52·83
	100·00	100·00	100·00

To distinguish between these three bodies, Gilmer prepared a crystalline baryta-derivative. Between $C_6H_{12}Ba_2O_6$ and either $C_5H_{10}Ba_2O_5$ or $C_7H_{14}Ba_2O_7$ there is a difference of from 1·5 to 2 in the percentage of carbon, so that an analysis is capable of determining the difference. Gilmer has fixed upon the formula $C_6H_{12}Ba_2O_6$, and consequently he writes $C_6H_{14}O_6$ for melampyrin.

We have been, for some time back, investigating the action of hydriodic acid upon different members of the sugar and mannite group. On the present occasion, we publisn our experiments on

* Proceedings of the Royal Society of Edinburgh, 1861–62.

† Ann. Ch. Pharm. cxxiii, 372.